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SEALED LITHIUM INORGANIC ELECTROLYTE CELL

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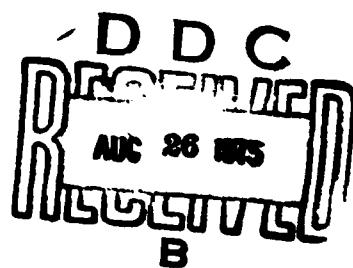
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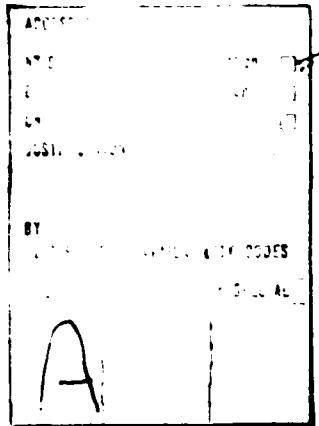
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electrolyte studies were continued using the standard size D cell as a test vehicle in an effort to establish the influence of various impurities on the passivation of lithium anodes. Impurities usually found in raw thionyl chloride, such as Cl₂ and SO₂, have been purposely added to the electrolyte to enhance any effect they might have on the lithium passivation. A rapid loss in the cell capacity in Cl₂ containing electrolyte has been observed as a result of lithium corrosion. The cells showed the usual passivation in this electrolyte following the exhaustion of the chlorine in the		

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corrosion reaction. The excess of SO₂ in solution showed no effect on lithium passivation.

An excess AlCl₃ have been added to the electrolyte, knowing that it would attack lithium surface and prevent the passivation for as long as there is an excess of AlCl₃ in the electrolyte. The corrosion reaction proved to be too fast and the cell behavior appeared to be similar to that observed with an excess of Cl₂.

Iron impurities usually come to the electrolyte with AlCl₃. A substantial increase in the cell voltage delay has been observed in the presence of iron added to the electrolyte in the form of FeCl₃.

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1. INTRODUCTION

The tests carried out so far in this program have demonstrated that it is not possible to construct lithium cells that would be capable of high discharge rates after a prolonged storage without a time delay in establishing a stable operating voltage. It is certain now that the cause for the delay is the build up of a passivating film on lithium anode. Although the amount of lithium involved in the film build up is negligibly small, large apparent losses in cell capacity are observed whenever there are fixed voltage limits within which the cell has to operate. The maximum capacity obtained within these fixed voltage limits is independent of the discharge rate in the low rate region but begins to fall off rapidly with increasing discharge rates above certain limit. The maximum rate at which the entire cell capacity is obtainable seems to be shifting towards lower values with time of storage, more so at elevated temperatures as a result of the film build up on lithium anodes. The intrinsic stability of the electrochemical system, as measured by the real loss of capacity at low rates, have been demonstrated in numerous discharge experiments lasting up to 1¹ months,¹ however. In spite of the proven stability of the system there seems to be little one can do to slow down the deterioration of the cell rate capability caused by the build up of the passivating film. Preliminary tests indicated that the impurities in the electrolyte might be responsible for the excessive film build up, either those contained in the raw materials or those formed within an improperly constructed cell at the beginning of its storage life.

Cl_2 and SO_2 are formed by a slow thermal decomposition of the solvents used, more so with the use of SO_2Cl_2 than with SOCl_2 . Higher concentrations of Cl_2 and SO_2 than those found in aged solvents, have been used in this accelerated test program.

Iron species are introduced into the electrolyte mostly via AlCl_3 . They can also be formed in an improperly designed cell by corrosion of the cell hardware. We have added iron, in the form of FeCl_3 , to the electrolyte and tested the voltage delay of cells on discharge after storage.

Fusing of the high power cells appears necessary now and preferred to venting as a means for averting the explosion of cells discharged at excessive rates. Fuses had to be built into the cell structure rather than added externally for a more reliable operation and in order to preserve the external dimensions of the standard cell. Two types of fuses have been evaluated with a considerable difference in costs of construction and with different operating characteristics. However, both seem to operate satisfactorily.

2. TEST RESULTS WITH VARIOUS ELECTROLYTES

Standard size hardware have been used in the construction of test cells with various electrolyte. The electrode structure has been modified, however, to limit the surface area and the maximum available capacity of lithium anodes. The size of the anode was $2.0 \times 4.5 \times 0.03$ cm weighing 1.45 g, with the total surface area of 1.0 cm^2 . The theoretical anode capacity was 5.6 Ah. The cathode and separators and the volume of electrolyte were kept unchanged. The cell closing was done by crimping, with an additional potting seal to keep water vapors away from the seal area. The storage was done in constant temperature chambers for a predetermined period of time prior to the measurements of the cell voltage delay on discharge. Three various discharge currents were applied to the cell, 0.5, 1 and 2A, corresponding to three various anode current densities of 2.8, 5.6 and 11.2 mA/cm^2 . A total of 144 cells were built and tested fresh, after 1 month storage at room temperature, 55 and 72°C .

2.1 ULTRAPURE ELECTROLYTES

The electrolyte was prepared using the purest chemicals available. Triple distilled thionyl chloride was from Eastman Kodak. Lithium Chloride was from J. T. Baker Chemical Co. with 99.3% LiCl, 10 ppm of heavy metals as Pb, and 5 ppm of Fe. Aluminum Chloride was from Fluka A.G., purissimum grade, free of water and iron. Twenty-four cells were built and tested for voltage delay according to the test program shown in Table 1. The table also shows the voltage delay data obtained with these cells after one month's storage. The fresh cells and the cells stored at room temperature performed satisfactorily at these high discharge rates. However, the high temperature storage showed very long delays, and, in the extreme case at 72°C , the cells just could not be brought above the operating voltage of 2V at these discharge rates. The fresh cells and the cells stored at room temperature yielded the same capacity, when discharged at 200 mA following the voltage delay measurements. The average capacity obtained at this rate was 4.4 Ah above 2.0 V cut off line, which is about 20% below the figures corresponding to the amount of lithium present. The cells stored at elevated temperatures were open for inspection after the voltage delay measurements. The anodes were found intact, with no change in thickness or appearance. The passivating film on lithium surface was, obviously, too dense and too resistive to be removed at this high rate.

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TABLE 1
VOLTAGE DELAY WITH ULTRAPURE ELECTROLYTES,
TIME FOR RECOVERY TO 2.0V

Storage Days	Cell No.	Storage Temp. °C	Current Density mA/cm ²	Voltage Delay
0	139		2.8	0
	140			
	141		5.6	0
	142			0
	143		11.2	0
	144			0
30	145		2.8	0
	146			0
	147	25	5.6	5 sec.
	148			3 sec.
	149		11.2	3 sec.
	150			3 sec.
30	151		2.8	15 min.
	152			30 min.
	153	55	5.6	30 min.
	154			30 min.
	155		11.2	30 min.
	156			20 min.
	157		2.8	No Recovery
	158			
	159	72	5.6	No Recovery
	160			
	161		11.2	No Recovery
	162			

2.2 ELECTROLYTE WITH EXCESS CHLORINE

Gaseous chlorine was bubbled through our regular type electrolyte at slow rate at room temperature over night, with a tap water condensor mounted on the flask to minimize the loss of thionyl chloride carried by the gas stream. No change in volume has been observed as a result of the saturation of the electrolyte with chlorine, suggesting a limited solubility. No analysis of the electrolyte has been made to establish the exact solubility figure. The electrolyte was used to build 24 cells under identical conditions as in the preceding test. Fresh cells, as well as those stored at various temperatures for one month, were tested for voltage delay at the same three rates. The results are shown in Table 2.

The fresh cells were placed on discharge within 24 hours following the construction and the voltage delay measurements. A uniform discharge behavior at the rate of 200 mA was observed, but the capacity obtained was significantly lower than expected on the basis of the amount of lithium present. An average of 3.6 Ah showed a loss of over 1 Ah within a few days. The storage at room temperature for 1 month resulted in a further reduction in the cell capacity. The discharge at 200 mA, yielded an average value of the cell capacity of 3.2 Ah following the voltage delay tests. The voltage delay values are comparable to those obtained with regular electrolytes. The storage at 55°C resulted in a complete deterioration of the cell capacity yielding less than 1 Ah at 200 mA rate with four cells after only 17 days. Two cells, assigned to the voltage delay tests at 2A, did not even show the proper open circuit voltage at the end of the storage period. The storage at 72°C was also discontinued after 17 days. All cells were found inoperable. The post mortem showed intact cathodes and spent anodes.

It is generally concluded that the excess of chlorine in the electrolyte is highly detrimental to the stability of lithium anodes in thionyl chloride electrolyte. Although the exact concentrations were not known, it seems that the lithium corrosion is continued beyond the stoichiometric relations of chlorine and lithium involved as suggested by the results at 72°C where the entire amount of lithium dissolved.

2.3 ELECTROLYTE WITH EXCESS AlCl_3

The idea that a slightly more acidic electrolyte might be able to keep the lithium surface free from an excessive passivation has been tested in the next series

TABLE 2
VOLTAGE DELAY WITH EXCESS Cl₂ IN ELECTROLYTE
TIME FOR RECOVERY TO 2.0V

Storage Days	Cell No.	Storage Temp. °C	Current Density mA/cm ²	Voltage Delay
0	73		2.8	0
	74			0
	75		5.6	0
	76			0
	77			6
	78		11.2	0
30	79	25	2.8	12 sec. 6 sec.
	80			
	81		5.6	0
	82			1 sec.
	83		11.2	30 sec. 26 sec.
17	85	55	2.8	2 min.
	86			
	87		5.6	50 sec. 35 min.
	88			
	89		11.2	Failed Failed
17	91	72	2.8	Discontinued
	92			
	93		5.6	Discontinued
	94			
	95		11.2	Discontinued
	96			

of experiments. An electrolyte was prepared with a 10% excess of AlCl_3 over the amount required to match the concentration of LiCl . Although it was known that the large excess of AlCl_3 shows a direct attack on lithium, a moderate excess was hoped to show an acceptable corrosion rate, keeping the anode surface free from the excessive passivation. Twenty-four cells were built using the above type electrolyte and tested according to the program shown in Table 3, together with the voltage delay data obtained.

It is obvious from Table 3 that the excess AlCl_3 causes a rapid corrosion of lithium anode. The cells either showed no delay or they were heavily passivated, depending on the time period and the temperature of storage. Fresh cells were discharged at 200 mA following the voltage delay tests and yielded an average capacity well below that obtained from the cells with the regular electrolyte. An average of 3.6 Ah, in fact, is very close to the value obtained with the excess chlorine electrolyte under the same conditions. The results after storage at room temperature for 1 month are also similar to those obtained with the excess chlorine electrolyte. An average of 3.0 Ah was obtained. The storage at both 55 and 72° resulted in a total deterioration of the cell capacity, either for lack of lithium or for inability of the remainder of the anode to deliver the capacity at the operating voltage above 2V with these high discharge rates.

It is quite clear that the excess of AlCl_3 in the electrolyte cannot be tolerated. All of it has to be neutralized with LiCl , shifting this Lewis acid-base equilibrium as far as possible in the alkaline direction. In fact, an excess of LiCl in suspension seems like a good idea to avoid the use of acid electrolyte.

2.4 EXCESS SO_2

Lithium forms a passivating film of $\text{Li}_2\text{S}_2\text{O}_4$ in contact with SO_2 in organic electrolyte cells. Sulfur dioxide is found in aged thionyl chloride and also in sulfuryl chloride as a product of a slow decomposition of these compounds. It seemed of interest to the voltage delay studies to establish if an excess of SO_2 over the concentration found in thionyl chloride would have any effect on the rate of formation or on the conductive characteristics of the passivating film in lithium cells with thionyl chloride electrolyte. SO_2 gas was bubbled overnight through a batch of regular thionyl chloride electrolyte until saturated under similar conditions as in the previously described preparation of the electrolyte with excess chlorine. The exact concentration of SO_2 reached has not been analyzed in this test but, according to a recent study² the concentration at room temperature could have been as high as 0.76 moles/l. Cells were

TABLE 3
VOLTAGE DELAY WITH 10% EXCESS OF AlCl_3 IN ELECTROLYTE
TIME FOR RECOVERY TO 2.0V

Storage Days	Cell No.	Storage Temp. $^{\circ}\text{C}$	Current Density mA/cm^2	Voltage Delay
0	49		2.8	0
	50			0
	51		5.6	0
	52			0
	53		11.2	0
	54			0
30	55	25	2.8	14
	56			11
	57		5.6	29
	58			14
	59		11.2	No Recovery
	60			
	61	55	2.8	
	62			
	63		5.6	No Recovery
	64			
	65	72	11.2	
	66			
	67	72	2.8	
	68			
	69		5.6	No Recovery
	70			
	71		11.2	
	72			

built using the SO_2 saturated thionyl chloride electrolyte and tested according to the program shown in Table 4 along with the voltage delay data obtained.

Fresh cells and those stored at room temperature for 1 month did not show any voltage delay at these high rates of discharge. The cell behavior is similar to that observed with ultrapure electrolytes as well as with our regular electrolyte prepared with care. The elevated temperature storage does not seem to have been affected significantly by the presence of SO_2 . One could actually see no difference in the voltage delay characteristics between these and the cells made with pure electrolytes.

The discharge at 200 mA following the voltage delay tests showed that SO_2 has no effect on the capacity obtained after storage either. Fresh cells, those stored at room temperature and those stored at 55°C for 1 month, all delivered an average capacity that is the same as the value obtained with regular fresh cells. A slight improvement has been observed at the extreme storage temperature of 72°C . Of the six cells involved, three were found with poor internal contacts and the remaining three delivered an average of 4.14 Ah.

2.5 IRON IMPURITIES

Iron is always found in commercial grade AlCl_3 in concentrations that could reach 70 ppm. Cell hardware might contribute to the contamination of the electrolyte with iron by corrosion, or it could be introduced by the solvent itself. A batch of electrolyte was prepared with 200 ppm of iron added in the form of FeCl_3 . Cells were made and tested according to the program shown in Table 5 along with the voltage delay data obtained.

As the data in Table 5 shows, iron species in the thionyl chloride electrolyte produced the strongest negative effect so far on the passivation of lithium anodes. The fresh cells, placed on discharge within 24 hours after assemblage, already showed in some cases an excessive passivation. The discharge at 200 mA showed that more than half of the cell capacity was unavailable at this rate at the operating voltage higher than 2.0V. Apparently, the post mortem showed a heavy dark brown layer on intact lithium anodes. It is obvious that iron must have deposited on the lithium surface and formed a passivating layer with poor conductive characteristics. The concentration of iron used in these experiments was obviously, very high. The results suggest, however, that iron species present even in low concentrations could produce the same effect over a longer period of time and with a high ratio of electrolyte volume to the total lithium surface area available.

TABLE 4
VOLTAGE DELAY WITH EXCESS SO₂ IN ELECTROLYTE
TIME FOR RECOVERY TO 2.0V

Storage Days	Cell No.	Storage Temp. °C	Current Density mA/cm ²	Voltage Delay
0	25		2.8	0
	26			0
	27		5.6	0
	28			0
	29		11.2	0
	30			0
30	31		2.8	0
	32			0
	33		5.6	0
	34			0
	35		11.2	0
	36			0
30	37		2.8	3 min. 5 min.
	38			
	39		5.6	9 min. 6 min.
	40			
	41		11.2	No Recovery
	42			
	43		2.8	
	44			
	45		5.6	No Recovery
	46			
	47		11.2	
	48			

TABLE 5
VOLTAGE DELAY WITH 200 ppm OF Fe IN SOLUTION
TIME FOR RECOVERY TO 2.0V

Storage Days	Cell No.	Storage Temp. °C	Current Density mA/cm ²	Voltage Delay
0	97		2.8	0
	98			0
	99		5.6	No Recovery 36 sec.
	100			
	101		11.2	No Recovery
	102			
30	103		2.8	No Recovery 1 min.
	104			
	105		5.6	No Recovery
	106			
	107		11.2	No Recovery
	108			
	109		2.8	No Recovery
	110			
	111		5.6	No Recovery
	112			
	113		11.2	No Recovery
	114			
	115		2.8	No Recovery
	116			
	117		5.6	No Recovery
	118			
	119		11.2	No Recovery
	120			

3. STORAGE AFTER PARTIAL DISCHARGE CELLS

Our regular type electrolyte, prepared with care, was used in the next series of experiments, whereby the cells were partially discharged before they were put on storage. Fresh cells of this group were all discharged for 1 hour with 1A constant current, which amounts to approximately 20% of the total cell capacity available in the lithium anode. After the storage of 1 month the cells were tested for voltage delay according to the program shown in Table 6.

The voltage delay data obtained with these cells are the best so far. All cells established a stable operating voltage above 2.0V after 3.5 minutes maximum after 1 month storage at 72°C, which in all other experiments produced totally passivated cells. This confirms previous experience with thionyl chloride cells, showing a much lower rate of passivating film build up with cells that were briefly used in various devices and then turned off and left alone. One could speculate as to the origin of this phenomenon but at least two factors appear certain. The first is the increase of the roughness factor of lithium surface by anodic etching at the beginning of discharge. Extruded lithium foil, and particularly a rolled one, came from the manufacturer in a very shiny form while a partially discharged foil acquires a dull appearance even in the ultrapure electrolytes. The second factor is the formation of the supersaturated solution in the vicinity of lithium surface in the course of discharge. It is quite possible that some of the impurities may be removed from the solution either in the course of discharge or when the supersaturated solution of lithium species finally breaks up and LiCl precipitates within the cathode pores.

These results deserve more attention. It would be of interest to establish the minimum fraction of prior discharge that would still show this effect and also the most favorable conditions under which the prior discharge is conducted. It might be possible to come up with a procedure that would be practical in reducing the voltage delay. The discharge, at 200 mA following the voltage delay measurements, yielded the expected cell capacities for each of the storage temperatures above the cut off voltage of 2.0V. There was no indication of any unexpected capacity deterioration on storage following the partial discharge.

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TABLE 6
 VOLTAGE DELAY AFTER STORAGE OF PARTIALLY DISCHARGED CELLS
 TIME OF RECOVERY TO 2.0V STORAGE TIME 30 DAYS

Cell No.	Storage Temp °C	Current Density mA/cm ²	Voltage Delay
121	25	2.8	0
122			0
123		5.6	12 sec.
124			6 sec.
125		11.2	12 sec.
126			12 sec.
127	55	2.8	2 min.
128			1 min. 18 sec.
129		5.6	2.5 min.
130			1 min. 15 sec.
131		11.2	4 min. 25 sec.
132			4 min.
133	72	2.8	2 min. 30 sec.
134			2 min. 48 sec.
135		5.6	2 min.
136			3 min.
137		11.2	3 min. 30 sec.
138			3 min.

4. FUSING OF D CELLS

High power type cells with the wound electrode structure are capable of discharge at rates far in excess of the maximum discharge rate at which an equilibrium is reached between the heat generation and the cooling of the cell. As a consequence, there is a steady rise in the cell temperature during discharge, reaching the point where the internal pressure build up causes an explosion. Calculations have been presented earlier,³ establishing the dependence of the maximum allowable discharge rate on the cell size and geometry. For the purpose of limiting the maximum discharge rate to the values lower than the critical ones, we have developed two types of internal fuses. Accidental short circuit or an intentional attempt to discharge the cell at the rate above the set limit will result in melting of the fuse and breaking the connection between the cathode and the cell positive terminal. Of the two choices given, we have decided in favor of an internally placed fuse with the understanding that an accidental short circuit will mean a loss of the cell. The externally placed replaceable fuse would probably be justified only on larger units, not required to conform to any dimensional standards. Two different types of fuses were developed and tested both satisfactorily. However, only one of them seems entirely feasible.

Preliminary tests were carried out with a simple nickel wire sealed in a glass ampule, as schematically shown in Figure 1. The fuse was connected to the cathode section of the circuit and physically placed in the hollow center of the wound structure. It is approximately 0.1 inch in diameter and 1.0 inch long, with two covar leads for connection to the cathode tab and the cell positive terminal. A 0.003" diameter nickel wire, for example, will sustain the discharge at 1A but will melt instantaneously at 1.4A. The higher limits of current are established by heavier gage wires that have to be selected on the basis of experiments in actual cells. The major deficiency of these fuses is a considerable rate of heat generation at values of current slightly below the critical one, due to the high melting point of nickel. Other materials were not applicable in this configuration, since they melted in the process of sealing the glass ampule. For this reason a different design of the fuse has been developed, enabling the use of the standard value commercial low melting fuses. This more advanced version of the cell fuse is shown in Figure 2.

The standard 3A small fuse was built into the cell cover hermetically separated from the electrode compartment, as well as from the outside of the cell. A flat round disc, with the glass feedthrough in the center was developed for other uses (semiconductor

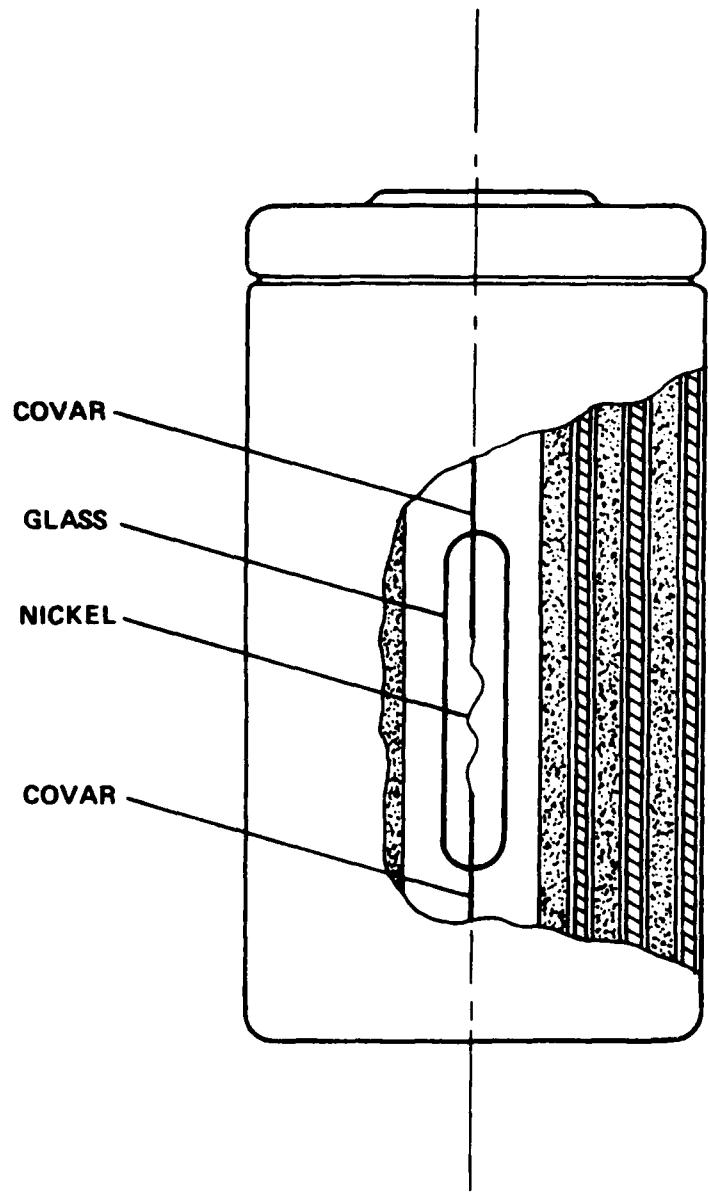


Figure 1. D Cell Fuse-1

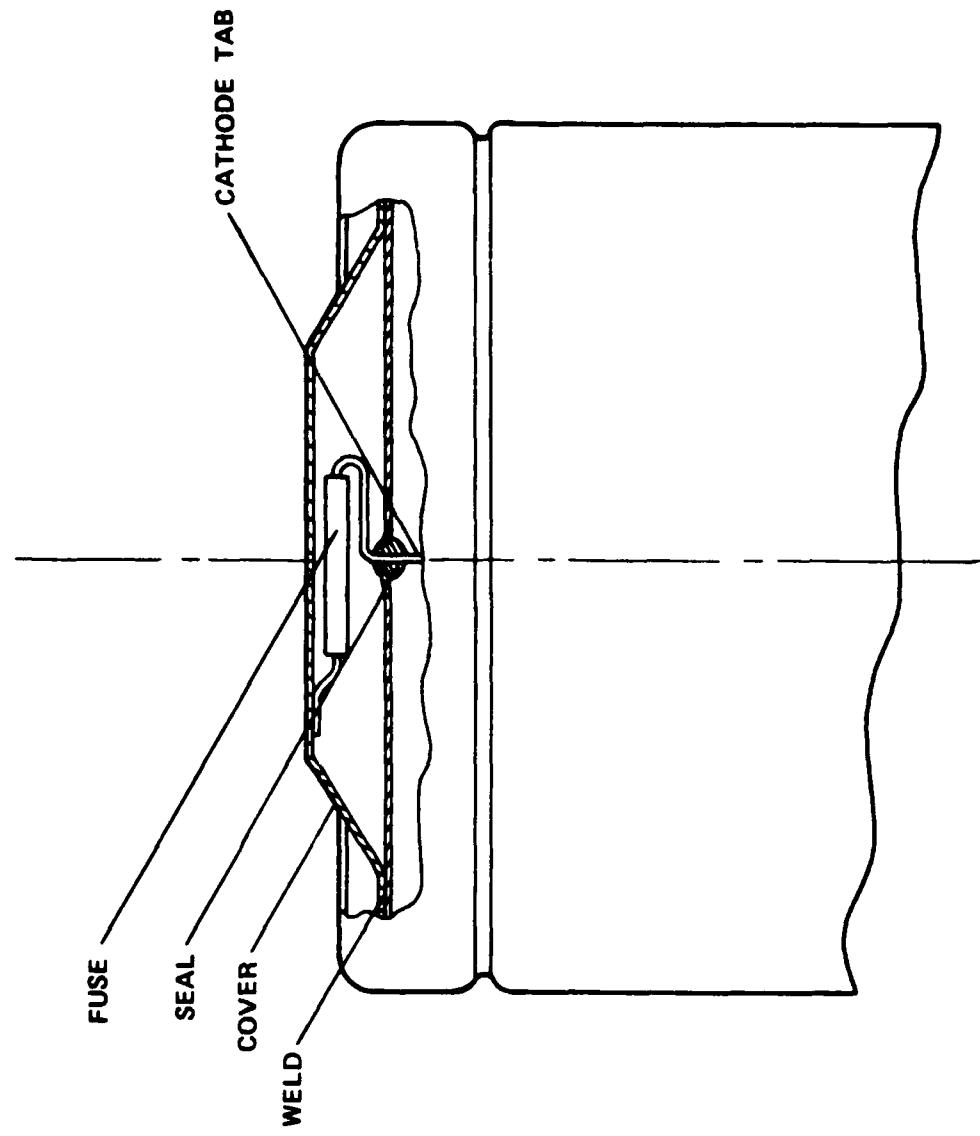


Figure 2. D Cell Fuse-2

devices and has been adapted for fusing of single cells. The disc is hermetically welded to the internal side of the cover, after the fuse was connected to the cover and the feedthrough pin. The cathode tab is spot welded to the opposite side of the pin in the cell assembling operation. The particular type of fuse used in these tests will sustain 3A discharge for 1 hour maximum, will melt in 15 seconds at 4A and in 5 seconds at 6A, which seem close to the requirements for the protection of size D cells. Other values of fuses are also available in the same dimensions that can conveniently be placed inside the dimple of our D cell cover.

5. VENTING OF D CELLS

A controlled release of gases and liquids must be facilitated, when an unfused cell is discharged at an excessive rate, in order to prevent a violent bursting of the pressurized cell container. Several different types of vents have been considered in the course of this development, but only one has, in fact, been tested. The engineering solution for a similar problem in the building of vented Ni-Cd cells seemed applicable to the lithium inorganic batteries as well. A schematic presentation of the vent construction is shown in Figure 3. A triangular hole is punched in the cell cover from outside, cutting only two sides of the triangle and leaving the spike facing inward. A 0.005" nickel membrane was stretched across the cover internal side and crimped over the cover edges. This cover was used to build the cells that were tested under short circuit conditions. Originally, the covers were built to release gases in the Ni-Cd cells at approximately 150 psi internal pressure. We have built empty cells using these covers, provided with a welded tube in the bottom of the can for testing under air pressures. A positive release was obtained at the pressures never exceeding 200 psi. Several complete cells, built with these covers were tested under short circuit conditions and the vents operated satisfactorily.

It has not been decided yet whether to build the cells for delivery under this program with the fuse or with the vents or both. Adding the peculiarities of the hermetic seal to the requirements for vents and fuses would make the cell top quite a complex subassembly. More tests might be necessary before it can be decided if both of these protective devices are really necessary.

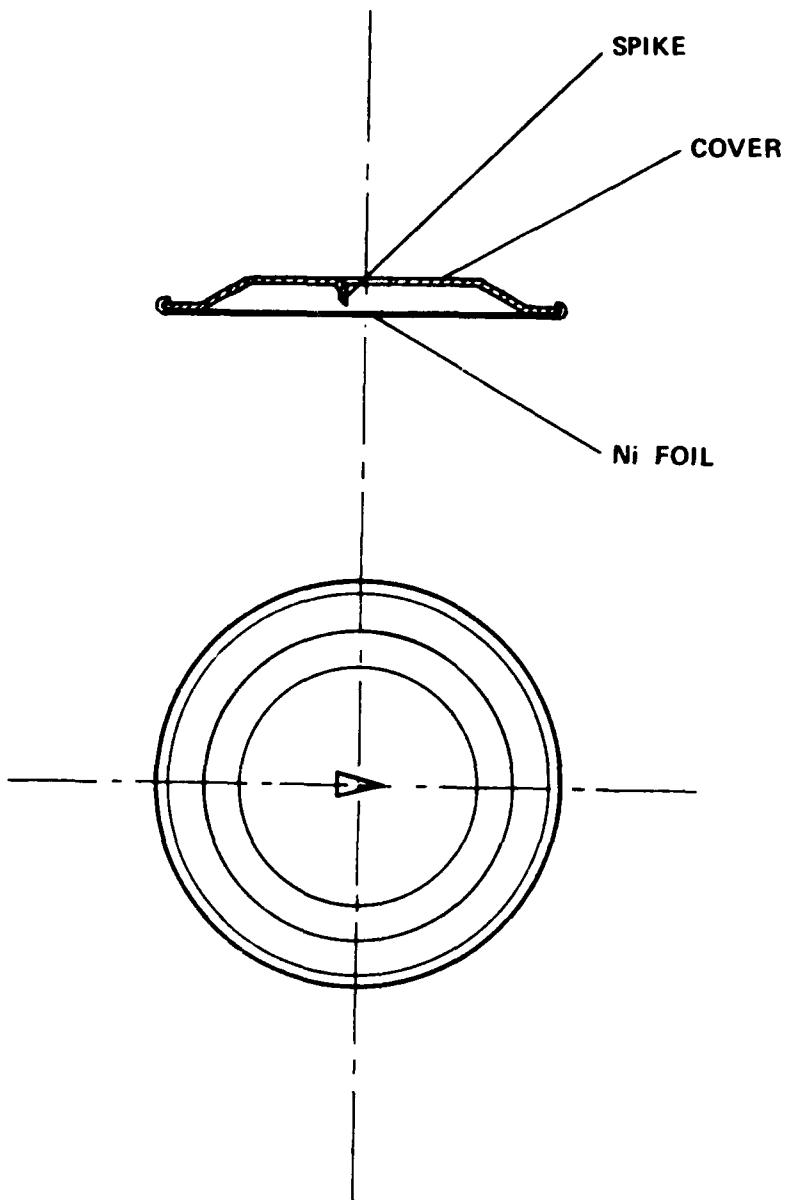


Figure 3. Cell Top with Vent

6. NEXT QUARTER PROGRAM

Several more fusing and venting tests will be performed in the next month, before the decision is reached as to which of the devices will be incorporated into the deliverable cells.

The economic feasibility of the hermetic cell closure has been proven and the hardware components have been ordered. The technology of the hermetic closures have been a standard practice in our facility, although not so much on the D size cell. No difficulties are expected in modifying the equipment and the procedures for use with this size cell.

Hermetic seal could be easily combined with either the fuse or the vent, but becomes a complex problem when both of these protective devices are employed in the same cell. Tests will show in the next month whether this degree of overprotection is really necessary.

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